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Molecular Organization of Bis-urea Substituted Thiophene Derivatives at the Liquid/Solid Interface Studied by Scanning Tunneling Microscopy

A. Gesquière, M. M. S. Abdel-Mottaleb, S. De Feyter,* and F. C. De Schryver*

University of Leuven (KU Leuven), Department of Chemistry, Laboratory of Molecular Dynamics and Spectroscopy, Celestijnenlaan 200-F, 3001 Heverlee, Belgium

F. Schoonbeek, J. van Esch, R. M. Kellogg, and B. L. Feringa

University of Groningen, Laboratory of Organic and Inorganic Molecular Chemistry, Nijenborg 4, 9747 AG Groningen, The Netherlands

A. Calderone, R. Lazzaroni, and J. L. Brédas†

Service de Chimie des Matériaux Nouveaux, Centre de Recherche en Electronique et Photonique Moléculaires, Université de Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium, and Department of Chemistry, The University of Arizona, Tucson, Arizona 85721-0041

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In this contribution we report on a structural investigation of the two-dimensional (2D) supramolecular organization of three bis-urea substituted thiophene derivatives, containing one, two, or three thiophene units, at the solution/graphite interface with scanning tunneling microscopy (STM). The compounds under investigation form highly ordered physisorbed monolayers. It is found that hydrogen bonding between the urea groups of adjacent molecules controls the spatial arrangement on the graphite surface. Molecular modeling and theoretical calculations demonstrate that the thiophene rings are tilted with respect to the surface and have partially overlapping π -systems. This control of the 2D self-assembly is promising for future studies on the electronic properties of these molecules.

Introduction

Scanning tunneling microscopy (STM) is a powerful tool for the investigation of ordered adlayers on a solid substrate at the molecular level. These highly ordered thin films, in most cases even monomolecular layers, have been studied extensively over the years. Particularly, organic monolayers formed by physisorption on weakly interacting substrates are of great importance in many processes occurring at interfaces such as lubrication, adhesion, and molecular recognition. Furthermore, the study and understanding of the interactions at play in adsorption processes on surfaces opens up a pathway toward a controlled patterning of surfaces on a molecular scale. One of the possible approaches in creating self-organized organic monolayers is the formation of those adlayers by adsorption from a solvent onto the solid substrate, which is the technique used by our research group. This type of monolayer has been studied for a wide variety of compounds. Besides functionality,¹ chirality,²

photoreactivity,³ and dynamics⁴ have also been investigated at the liquid/solid interface.

Thin films of conjugated oligomer and polymer systems have become a subject of great interest over the recent years due to their possible application in optical and electronic devices.⁵ Polythiophene is an important prototype for conducting polymers.⁶ The study of the self-assembly of thiophene derivatives could lead to the development of new films with novel physical properties.

* To whom correspondence should be addressed. E-mail addresses: frans.deschryver@chem.kuleuven.ac.be and steven.defeyter@chem.kuleuven.ac.be.

† The University of Arizona.

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These properties can be controlled in a chemical way by changing the length and the substituents of the thiophene derivatives. The two-dimensional organization at the liquid/graphite interface of a monothiophene functionalized in the β -position with a long alkyl chain was imaged by Fukunaga et al.⁷ The molecules were found to be lying head-to-head, with the thiophene rings oriented diagonally on the HOPG (highly oriented pyrolytic graphite) surface and stacked face to face. Bäuerle et al. imaged a homologue series of oligothiophenes with alkyl substituents in the β -position with STM at the liquid/solid interface.⁸ They observed a two-dimensional (2D) organization that depends on the length of the oligothiophenes. The 2D arrangement of a series of alkylated sexithiophenes has also been investigated at the liquid/graphite interface.⁹ The influence of an increasing polarity of the substituents on the monolayer structure of oligothiophenes physisorbed on graphite has been investigated by Stecher et al.¹⁰ Other studies on physisorbed oligothiophenes and the influence of length and substituents on the 2D organization have also been reported.^{11–13} A few studies also deal with the organization of thiophene derivatives in chemisorbed adlayers on Cu(110)¹⁴ and Ag(111).¹⁵

Aside from the chemical modifications that can be made to individual molecules in order to change their physical properties, Garnier et al. have shown that by increasing the molecular order in thin films of sexithiophenes the mobility of charge carriers can also be enhanced.¹⁶ A controlled molecular arrangement can be achieved by physically creating ordered thin films, for example by the Langmuir–Blodgett technique or evaporation in UHV onto a substrate. The spatial arrangement can also be governed by self-recognition properties, for example based upon hydrogen bond formation. In this way a well-defined supramolecular organization can be obtained that is controlled by hydrogen bond interactions. We used the latter approach to generate closely packed 2D arrays of thiophenes at the liquid/solid interface by means of introducing urea groups in the alkyl substituents of the thiophenes. A detailed STM study on alkyl-substituted bis-urea derivatives has previously been reported by our research group.¹⁷ The monolayers formed by these compounds are remarkably stable, even allowing the imaging of isolated lamellae with submolecular resolution. The 2D structure was found to be clearly dominated by the hydrogen bond interaction between the urea groups.

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The bulk properties of the bis-urea substituted thiophene derivatives under consideration in this paper have previously been investigated.¹⁸ In solution the molecules form a one-dimensional (1D) framework, controlled by intermolecular hydrogen bonds between the urea groups, in which the thiophene moieties are π -stacked. With pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) experiments it has been shown that this arrangement provides an efficient path for charge transport within these self-assembled fibers.

In the present paper we discuss our findings about the 2D organization of three bis-urea substituted thiophene derivatives at the liquid/graphite interface. Our STM results are corroborated by molecular mechanics calculations and molecular dynamics simulations.

Experimental Section

Scanning Tunneling Microscopy. Prior to imaging, all compounds under investigation were dissolved in 1-octanol (Aldrich, 99%) and a drop of this solution was applied on a freshly cleaved surface of highly oriented pyrolytic graphite. The concentrations of the solutions of T1, T2, and T3 are 1.0×10^{-3} M, 4.2×10^{-3} M, and 2.7×10^{-3} M, respectively. The STM images were acquired in the variable current mode (constant height) under ambient conditions with the tip immersed in the liquid. In the acquired STM images, white corresponds to the highest and black to the lowest measured tunneling current. STM experiments were performed using a Discoverer scanning tunneling microscope (Topometrix Inc., Santa Barbara, CA) along with an external pulse/function generator (Model HP 8111 A), with negative sample bias. Tips were electrochemically etched from Pt/Ir wire (80%/20%, diameter 0.2 mm) in a 2 N KOH/6 N NaCN solution in water.

The experiments were repeated in several sessions using different tips to check reproducibility. Different settings for the tunneling current and the bias voltage were used, ranging from 0.3 to 1.0 nA and -10 mV to -1.5 V, respectively. The unit cell parameters were not affected by the difference in experimental conditions. After registration of an STM image of a monolayer structure, the underlying graphite surface was recorded at the same position by decreasing the bias voltage, serving as an in-situ calibration. During imaging, we detected little drift of the STM system, and care was taken that the same region of the monolayer was imaged during consecutive scans. All STM images contain raw data and are not subjected to any manipulation or image processing.

Synthesis

The synthesis of the compounds under investigation has been described elsewhere.^{17a,19}

Molecular Mechanics Calculations: Methodology. The molecular mechanics and molecular dynamics calculations have been performed with the Cerius² package developed by Molecular Simulations Inc. The potential energy is described with the Dreiding force field,²⁰ which is a simple generic force field capable of providing accurate geometries for organic, biological, and main-group inorganic systems. It uses general force constants and geometry parameters based on simple hybridization considerations; furthermore, it contains explicit hydrogen bond terms. The long-range nonbonded interactions are calculated by using

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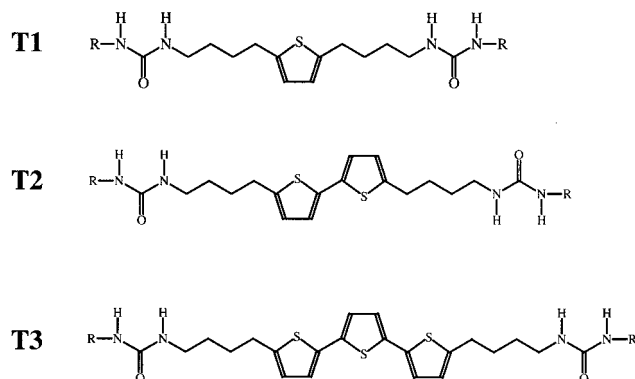


Figure 1. Chemical structure of T1, T2, and T3. R = C₁₂H₂₅.

the Spline method with spline-on and spline-off parameters set to 15.00 and 19.00 Å, respectively. In fact, within the spline-on–spline-off range, the nonbonded interactions are attenuated, and beyond spline-off, they are neglected. During the geometry optimizations, the atomic charges are calculated every 250 optimization steps by using the charge equilibration approach of Rappé and Goddard;²¹ this is a general scheme for predicting charges of large molecules on the basis of only geometry and experimental atomic properties. This approach allows the charges to respond to changes in the environment of the atom and can be applied to any compound (metal, polymer, ceramic, biological). In the case of the T1 derivative (molecular structure shown in Figure 1), molecular dynamics simulations have been performed on the structure optimized at the molecular mechanics level. These simulations rely on an NVT ensemble with the temperature set at 300 K for 1000 ps run times. The considered plane of graphite is composed of 20*20 fused rings and contains 840 atoms. The atomic positions are fixed during the energy minimization process. Note that this choice of size makes edge effects negligible.

Results and Discussion

A. STM Results. The two-dimensional ordering of three bis-urea substituted thiophene derivatives has been studied by means of STM at the liquid/graphite interface. The molecular structure of the compounds under consideration is depicted in Figure 1. Each bis-urea derivative in a lamella can form up to eight hydrogen bonds with adjacent molecules. Hence, a stable supramolecular organization can be observed with submolecular resolution during the STM experiments. In Figure 2a an STM image of a physisorbed monolayer consisting of T1 molecules is shown. The molecules are arranged in lamellae that have a width of 51.8 ± 1.4 Å. Within a lamella three bright rows can be discerned. In this context bright refers to a higher detected tunneling current relative to the current measured over the alkyl chains, which appear with darker contrast in STM images. The central bright line in a lamella corresponds to the location of the thiophene groups (red arrow). Theoretical calculations suggest that a higher tunneling current will be detected over aromatic moieties.²² It has been experimentally confirmed that this is indeed a general trend. The bright rows left and right of the thiophene groups coincide with the location of the urea groups within a lamella (yellow arrows). This observed contrast is in agreement with observations made by Takeuchi et al. for amide groups and has been reported previously by our research group.^{17,23} In contrast to the case for Langmuir–Blodgett films, the molecules are oriented with their molecular axes parallel to the graphite

surface and form hydrogen bonds with adjacent molecules within a lamella, thus stabilizing the lamellar structure. From a detailed analysis we find that the intermolecular distance is 4.62 ± 0.05 Å. This implies that this distance is being directed by hydrogen bonding between two successive urea groups of neighboring molecules.²⁴ The intermolecular distance could be accurately determined since in a number of acquired images a Moiré pattern could be observed (not shown).²⁵ The appearance of this contrast modulation (in our case along the lamellar axis) implies that not all of the alkyl chains are located at equivalent adsorption sites. The Moiré period contains six molecules. The molecular model in Figure 2b gives a visual representation of the monolayer structure based on the packing parameters obtained from the data analysis.²⁶ The thiophene rings cannot lie completely flat on the graphite surface due to steric hindrance with the adjacent thiophene rings. This finding is corroborated by the theoretical calculations, which are discussed in section B.

Figure 3a shows a typical STM image of a densely packed T2 monolayer adsorbed from a solution in 1-octanol onto the graphite substrate. A molecular model of the observed structure is shown in Figure 3b.²⁶ The molecules are arranged in lamellae that have a width of 56.8 ± 1.4 Å. The overall structure appears similar to that of a T1 monolayer. An important noticeable difference is that now in the center of a lamella two rows of bright spots can be discerned whereas for T1 this was one row (red arrow). The location of these bright spots corresponds to the location of the two thiophene rings. Note that those rows differ slightly in contrast in this particular image. At this time we attribute this to a scanning artifact. When the scanning direction was rotated 180° or when we simultaneously acquired forward and reverse scanned images, the shadowing effect reversed accordingly. The individual thiophene rings are more clearly visible in the STM image depicted in Figure 4. One can also notice in Figure 3a that the urea groups left and right of the thiophene groups have a different contrast (yellow arrows). This contrast effect has been previously reported for alkyl-substituted bis-urea derivatives with C₂ symmetry when adsorbed on graphite.¹⁷ In that case molecules with an even number of carbons in the alkyl spacer have urea groups that show a different contrast in STM images; this is related to the opposite orientation of the urea groups with respect to each other. On the other hand, molecules with an odd number of carbons in the alkyl spacer have urea groups that show the same contrast in STM images; in that situation the urea groups have the same orientation.¹⁷ However, this contrast effect has not been consistently observed for T1 and T2 in the collected STM data. We attribute this to the proximity of the urea groups to the thiophene moieties, which under our experimental conditions gives rise to an artificial shadowing effect, that is, lower detected tunneling current. In analogy with the case for compound T1, it was possible to observe a Moiré pattern in the direction of the lamellar axis in some cases (not shown). The Moiré period contains six molecules. The

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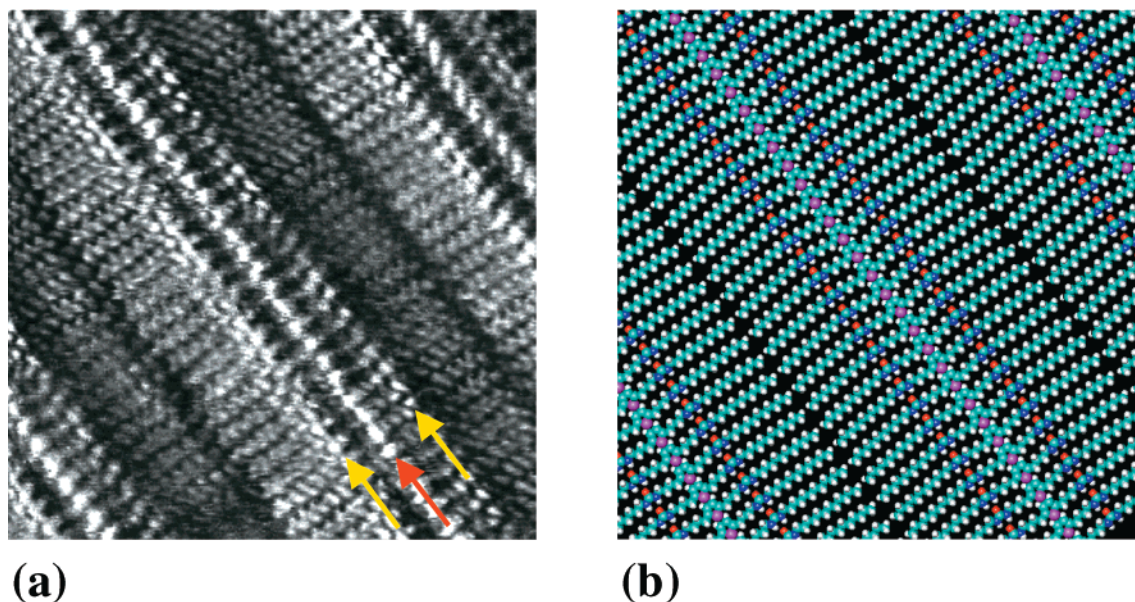


Figure 2. (a) STM image of a T1 monolayer formed by physisorption at the 1-octanol/graphite interface. The red arrow indicates the location of the thiophene rings within a lamella. The yellow arrows indicate the location of the urea groups. The image size is $9.7 \times 9.7 \text{ nm}^2$. $I_{\text{set}} = 1.0 \text{ nA}$, and $V_{\text{bias}} = 0.58 \text{ V}$. (b) Molecular model of the STM image shown in part a.

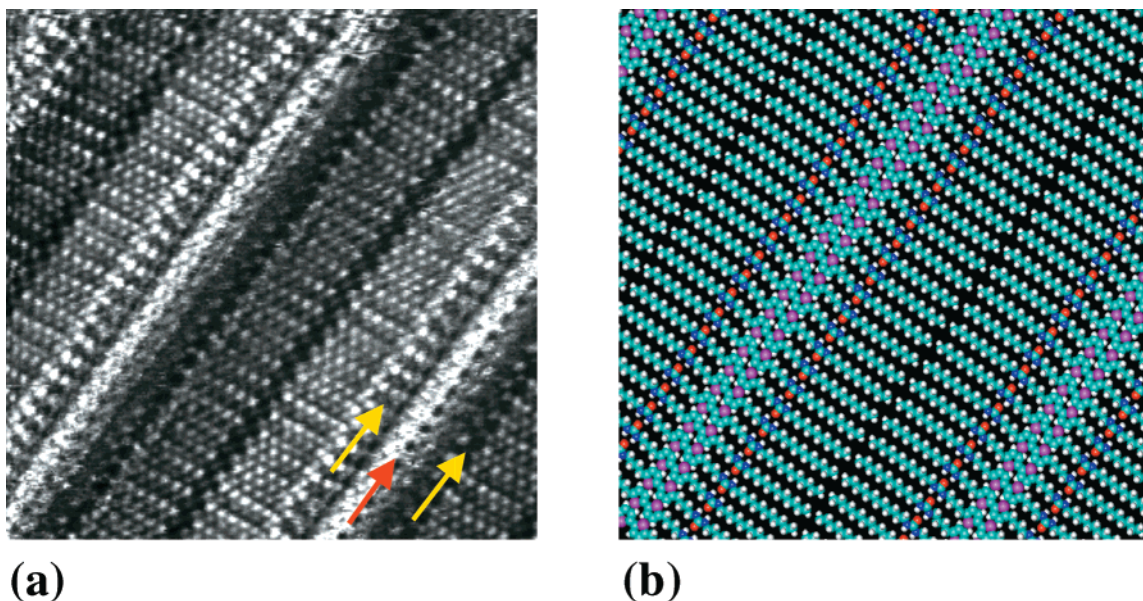


Figure 3. (a) STM image of an ordered T2 adlayer physisorbed at the 1-octanol/graphite interface. The red arrow indicates the location of the thiophene rings within a lamella. The yellow arrows indicate the location of the urea groups. The image size is $10.4 \times 10.4 \text{ nm}^2$. $I_{\text{set}} = 1.0 \text{ nA}$, and $V_{\text{bias}} = 0.60 \text{ V}$. (b) Molecular model of the STM image shown in part a.

intermolecular distance in this case was again $4.62 \pm 0.05 \text{ \AA}$. Thus, we can conclude that adjacent molecules within a lamella form hydrogen bonds. In addition, from molecular modeling (Figure 3b) we also find that the thiophene rings are not lying flat on the substrate but make an angle with the substrate surface.²⁶ This will be discussed further in the next section.

Finally, we also examined a third bis-urea thiophene derivative T3, an STM image of which is shown in Figure 5a. The same characteristics and contrast features as those for T1 and T2 can be discerned. The thiophene moieties are visible as a bright band in the middle of a lamella. In this particular image the dark troughs left and right of the thiophene rings in the lamella on the left correspond to the location of the urea groups. In the lamella on the right one of the urea rows has a bright contrast, while the other one has a dark contrast. The intermolecular distance,

which has been determined on the basis of the Moiré pattern that could be observed in some images (not shown), is $4.62 \pm 0.05 \text{ \AA}$. The lamellar width is $61.6 \pm 1.3 \text{ \AA}$. The packing arrangement is again clearly dominated by the hydrogen bonds that are formed between the urea groups. As with the other two bis-urea thiophene derivatives, the thiophene rings are spatially overlapping within a lamella (shown in the molecular model in Figure 5b)²⁶ and are tilted with respect to the graphite surface. When one looks consecutively at the STM images for T1, T2, and T3, it is noticeable that the thiophene part of the molecules becomes less resolved. This indicates increased dynamics in this region of a lamella, which is ascribed to a larger part of the molecule not being fully adsorbed on the graphite substrate.

When the results obtained for the bis-urea (α,α') substituted thiophene derivatives are compared to the

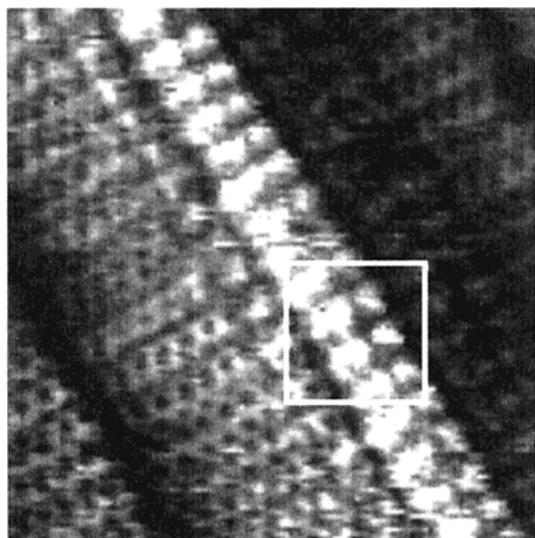


Figure 4. STM image of a T2 lamella. The two thiophene rings can be distinguished as two rows of bright spots in the center of the lamella. The image size is $6.0 \times 6.0 \text{ nm}^2$. $I_{\text{set}} = 1.0 \text{ nA}$, and $V_{\text{bias}} = 0.59 \text{ V}$.

examples reported in the literature, it becomes obvious that this system has quite unique characteristics. First of all, in our case we have successfully imaged α, α' -dialkylated oligothiophenes on graphite with true sub-molecular resolution in a large number of instances. This contrasts with reports by Stabel et al. and Azumi et al. that α, α' -dialkylated derivatives rarely, if at all, form stable monolayers on HOPG.^{9,12} The urea groups in the side chains have, as mentioned before, a highly stabilizing effect on the lamellar structures. Furthermore, the results reported by Azumi et al. show that their imaged α, α' -dialkylated oligothiophenes form 2D crystals on MoS_2 in which one of the alkyl side chains of a molecule is sandwiched between two thiophene units within a row.¹² The alkylated sexithiophenes of Stabel et al. have their thiophene units aligned along the lamella axis, but the distance between these groups ranges from 7.7 \AA to as much as 11.4 \AA .⁹ This indicates that the thiophene rings of adjacent molecules in a lamella are not spatially

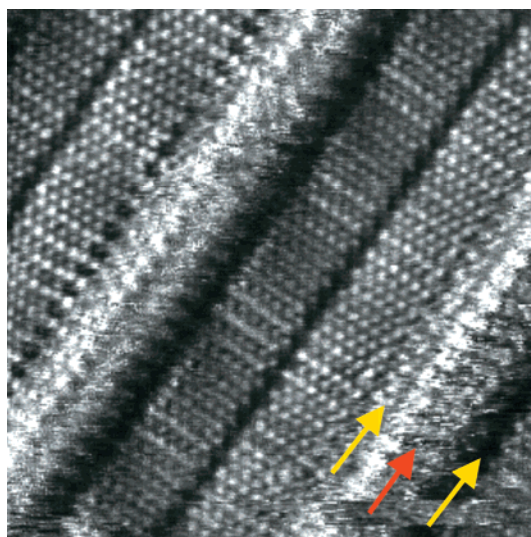
overlapping. The same holds true for the α -functionalized oligothiophenes published by Stecher et al.^{10,11} and the steroid-bridged thiophenes described by Vollmer et al.¹³ None of the compounds reported by Bäuerle et al. had their oligothiophene moieties π -stacked because of the steric hindrance arising from the alkyl substituents in the β -position.⁸

Thus, in all of these cases direct π - π stacking of the thiophene moieties is not observed when confined as physisorbed monolayers on surfaces. The only exception to this lack of π - π stacking was reported by Fukunaga et al. for a monothiophene functionalized in the β -position with a long alkyl chain.⁷

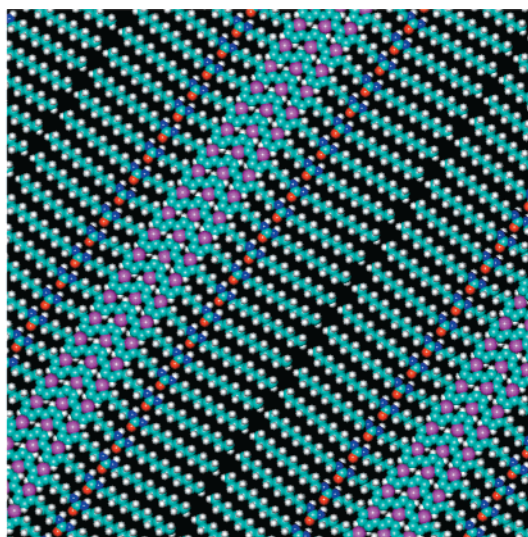
For the system described in this contribution however, we can conclude from the analysis of the experiments and the performed calculations that the thiophene rings are tilted with respect to the surface and are spatially overlapping within a lamella. As far as we know, this is the first report of oligothiophenes spontaneously self-assembling by physisorption on a substrate surface to form ribbons of spatially overlapping oligothiophenes.

B. Theoretical Results. To get a better understanding of the role of the intermolecular hydrogen bonding between the urea groups and its effect on the orientation of the thiophene rings with respect to the graphite surface, molecular mechanics and molecular dynamics calculations were carried out on T1 and T2, neglecting the outermost alkyl chains. As it was shown experimentally that the molecular order within a lamella is dominated by the hydrogen bonds formed between the urea groups, it is justified not to take into account the dodecyl groups.

For both T1 and T2, the starting system is composed of three chains deposited on the graphite plane in order to mimic a portion of lamella. The behavior of the central chain is expected to model the properties of a molecule within a lamella, while the two outer chains may show larger geometric relaxation due to the absence of neighbors. The initial distance between adjacent molecules is set to the value measured from the STM images, that is, 4.62 \AA . To study the effect of this close-packing on the torsion of the chains (and especially of the thiophene rings), we have first considered that they are fully planar and parallel to the graphite plane.



(a)



(b)

Figure 5. (a) STM image of a T3 monolayer formed by physisorption at the 1-octanol/graphite interface. The red arrow indicates the location of the thiophene rings within a lamella. The yellow arrows indicate the location of the urea groups. The image size is $10.3 \times 10.3 \text{ nm}^2$. $I_{\text{set}} = 1.0 \text{ nA}$, and $V_{\text{bias}} = 0.56 \text{ V}$. (b) Molecular model of the STM image shown in part a.

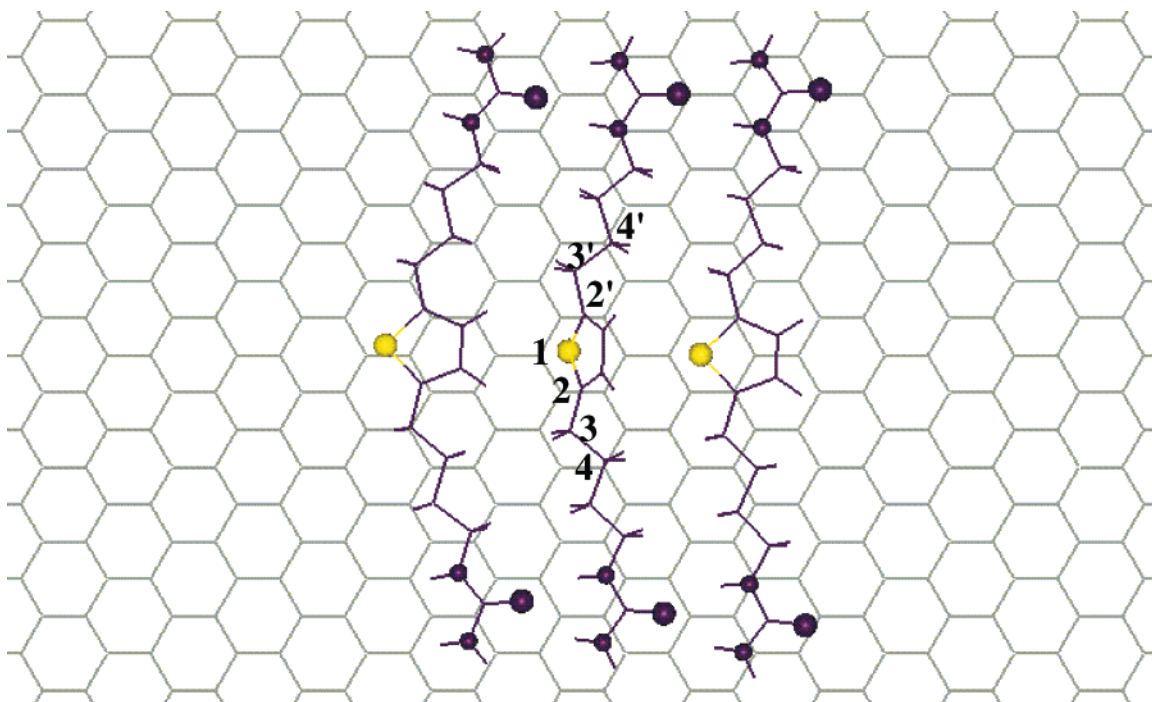


Figure 6. Top view of the molecular mechanics optimized structure of three T1 chains adsorbed on a plane of graphite.

For the T1 derivative, the optimization leads to the stable structure presented in Figure 6. A torsion appears inside the middle chain: the thiophene ring tilts away from the parallel adsorption, due to steric hindrance with the neighboring rings. This steric hindrance can only be relieved via the tilting of the thiophene ring because the molecules tend to remain closely packed (around 4.70 Å between the oxygen atoms) due to the locking of the hydrogen bonds between the urea groups. The torsion angle of the thiophene ring relative to the alkyl chains (which run parallel to the substrate) is 63°, with the sulfur atom pointing toward graphite. This orientation has been found to be more stable than its counterpart with the sulfur pointing away from the surface. The rings on the outer two chains remain quasi planar with respect to the rest of the chain. The relative conformation of the thiophene rings on the three molecules can be understood as being the best compromise between the π interaction of the ring with the graphite plane, which favors the flat conformation, and the steric hindrance between the rings, which induces tilting. In the three-molecule assembly, the most stable situation consists of the two outer rings almost flat on the surface and the central one significantly tilted, instead of all three rings moderately tilted. Nevertheless, the flat conformation of the outer rings is only possible because they correspond to the end of the "lamella" and do not experience steric hindrance on one side. It is expected that in longer lamellae all "internal" thiophene rings would be tilted.

We have also performed molecular dynamics simulations. They confirm the results obtained at the molecular mechanics level. As represented in Figure 7, throughout the simulation, the tilting of the thiophene ring relative to the rest of the molecule, in the middle chain, remains around 60° (the corresponding peak presenting some width); this is the same value as that obtained at the molecular mechanics level (Figure 6).

In the case of the T2 derivative, the optimization from the initially planar structure leads to the structure depicted in Figure 8. Again, the planarity is broken at the level of the thiophene rings of the middle chain, due to

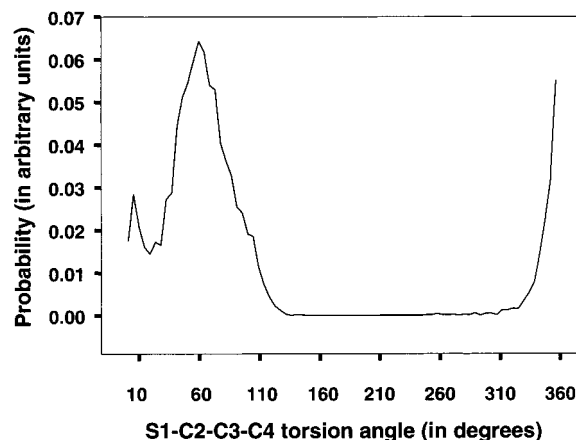


Figure 7. Probability of occurrence of the torsion angle of the thiophene ring of T1 (relative to the alkyl chains), in the middle chain, throughout the molecular dynamics simulation.

steric hindrance. The S1-C2-C3-C4 and S1'-C2'-C3'-C4' torsion angles (between the rings and the alkyl chains) are 48° and 32°, respectively. The S1 sulfur atom points toward the carbon surface while the S1' atom is oriented toward the opposite direction. Probably, the smaller torsion observed for the second ring (upper ring in Figure 8) is due to the steric hindrance of the two C β -H bonds, which does not allow for a large tilt. This is also consistent with the preferential orientation of the sulfur atom toward graphite observed in T1. The distances between the S1 or S1' atom and the plane of graphite are calculated to be 3.4 and 4.9 Å, respectively. It is to be noted that the two thiophene rings still lie practically in the same plane (the S1'-C5-C6-S1 torsion angle being 176.0°), with the C3-C4 and C3'-C4' bonds being slightly tilted away from the plane parallel to the graphite surface. Nearly no torsion is present in the outer two chains (S1-C2-C3-C4 and S1'-C2'-C3'-C4' torsion angle < 3.1°). The distance between adjacent chains is almost unchanged (around 4.7 Å between the oxygen atoms).

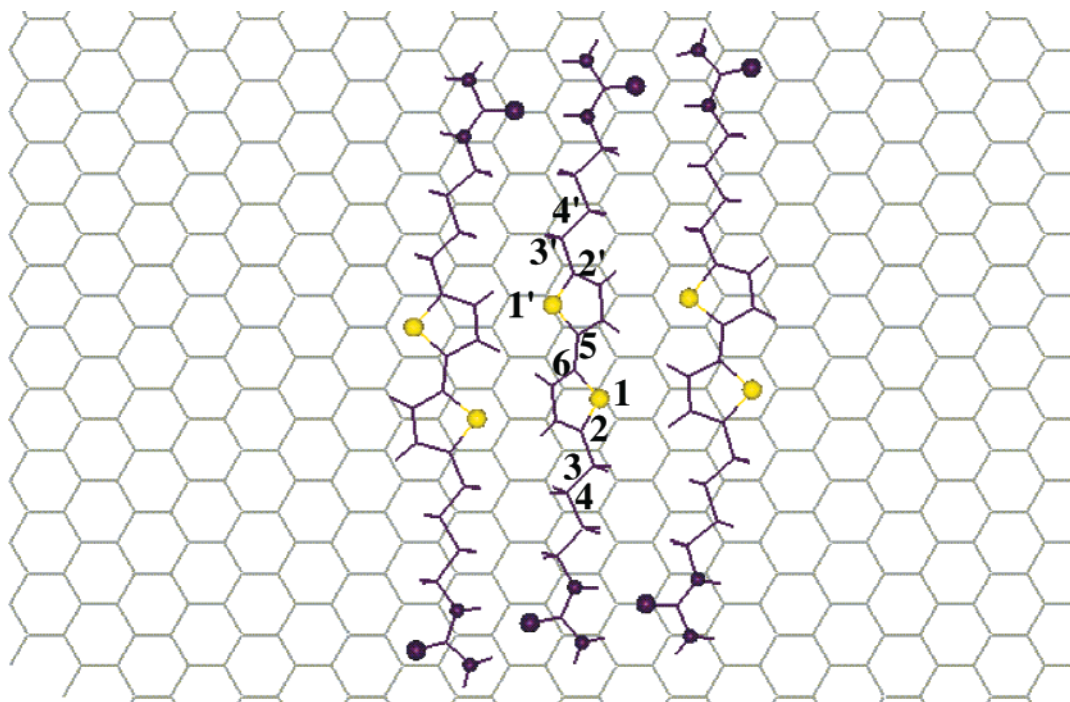


Figure 8. Top view of the optimized structure of three T2 chains adsorbed on a plane of graphite.

C. Conclusion. In this paper we have investigated the 2D supramolecular organization of bis-urea thiophene derivatives. For all bis-urea compounds that we investigated we found that, on the basis of the analysis of the observed Moiré patterns, the intermolecular distance is 4.62 ± 0.05 Å. This makes it clear that the spatial arrangement of the molecules on the graphite surface is controlled by the hydrogen bonding between the urea groups of adjacent molecules. From molecular modeling, molecular mechanics calculations, and molecular dynamics simulations, we have found that for this arrangement the thiophene rings cannot be parallel to the surface. Hence, the thiophene rings are tilted with respect to the surface and are spatially overlapping within a T1, T2, or T3 lamella. This makes these molecules interesting candidates for further investigation, specifically concerning their electronic properties in a 2D adlayer physisorbed on a substrate surface.

In summary, the bis-urea thiophene derivatives form a well-defined arrangement on HOPG that arises from the self-organization properties of the urea groups, which are based on hydrogen bonding.

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